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Soft norm-conserving pseudopotential for carbon

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Abstract. A soft, norm-conserving pseudopotential for carbon is presented and its performance tested by calculations on atomic states and on diamond: electronic energy levels of different atomic configurations, equilibrium lattice constant, bulk modulus, and the TA(X) frozen-phonon frequency are accurately reproduced. Convergence of the total energy of diamond with the size of the plane-wave basis set is compared for several frequently used pseudopotentials, and it is shown that calculations with the reported pseudopotential can be performed at considerably lower cost than with the other norm-conserving pseudopotentials, without loosing the accuracy of the latter in predicting structural and dynamical properties. The rapid convergence of the results with the plane-wave cutoff is comparable to the performance of the Vanderbilt's ultrasoft pseudopotentials. The transferability of the pseudopotential to other electronic configurations is discussed.

PACS. 71.20.-b Electron density of states and band structure of crystalline solids – 71.20.Ps Other inorganic compounds

1 Introduction

Application of *ab initio* methods to calculation of properties of complex materials has led in the past years to significant improvement in understanding material properties on atomistic level. Amid the different computational techniques, the ones working in plane wave basis and using pseudopotential to describe the electron-ion interaction are of particular importance and have numerous advantages. Among the most convenient features we note the unbiased representation of the wavefunction, controlled convergence, high calculational efficiency when used with up-to-date Fast-Fourier-Transform algorithms, and a straightforward implementation of the equations of motion of the Car-Parinello method. Although many attempts have been made in recent years to optimize the plane wave convergence of the pseudopotential calculations, improvements are still possible that considerably lower the cost of computations. In this paper we demonstrate on the example of carbon that one can construct norm-conserving pseudopotentials which significantly reduce the size of the plane-wave basis set required for obtaining converged and accurate results.

2 Method

We have applied to carbon the "phase-shift" technique for generation of soft pseudopotentials, that was proposed in reference [1]. This method creates generalized [2] norm-conserving l-dependent pseudopotentials "directly", without relying on the inversion of the Schrödinger equation. It is useful to remind that, as an alternative to that inversion, one might envisage the straightforward iterative searching for the matching logarithmic derivatives. However, it turns out that such an approach is inapplicable because of its numerical instability. An equivalent but numerically stable way suggested in reference [1] is to impose conditions on phase shifts and to find the pseudopotential satisfying these conditions by an iterative technique. An interesting feature of the procedure formulated in reference [1] is that it possesses additional "degrees of freedom", rather than the minimum indispensable for merely mimicking the all-electron results. These "redundant" parameters can then be used to make the pseudopotential satisfy some additional conditions: optimal smoothness, "computational efficiency" in plane-wave basis, or other requirements.

In the present case, we selected as reference-configuration of carbon the ground state $1s^2 2s^2 2p^2 3d^0$, and chose as reference energies the atomic eigenvalues; among several choices for the cutoff radii R_c, we retained the radius $R_\mathrm{c} = 2.0$ a.u. for $\ell = 0$ and $\ell = 1$ nonlocal

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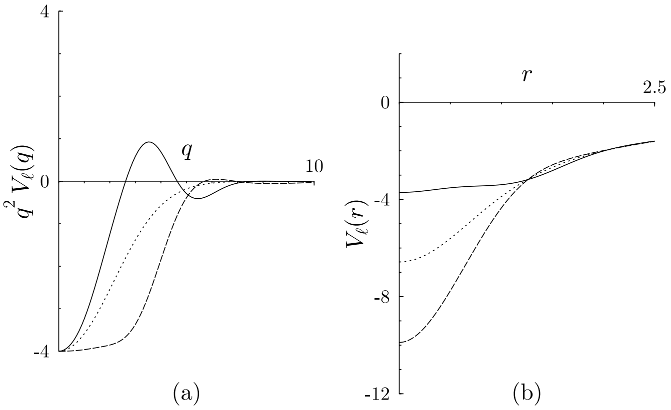
Table 1. Pseudopotentials generated in this work (Fig. 1), in hartree units, expanded in terms of Gaussian functions: the coefficients below have exactly the same meaning as the parametrization of the BHS pseudopotentials (Eqs. (2.21, 2.22) of Ref. [4]).

	core	$l = 0$	$l = 1$	$l = 2$
α_1	1.94980	1.23090	3.99920	1.
α_2	0.80800	1.11610	1.22790	1.
α_3		0.99750	1.16590	1.
c_1	1.12070			
c_2	−0.12070			
A_1		−8.5707323237E+04	1.0012285592E+00	0.
A_2		2.4476199271E+04	−1.0769391860E+04	0.
A_3		6.1233984224E+04	1.0765078640E+04	0.
A_4		−3.4670805459E+03	2.9558085596E+00	0.
A_5		−1.1396755049E+04	−3.4445382995E+02	0.
A_6		−2.2377639493E+03	−3.2109229790E+02	0.
Z	4.00000			



(a) (b)

Fig. 1. The present pseudopotential of carbon, in the reciprocal (a) and direct (b) spaces. Solid lines: s-component; dashed lines: p-component; dotted lines: the d-component (chosen as "local", *i.e.* to be applied to all $\ell \geq 2$). Atomic units (bohr and hartree) are used.

components. We choose $l = 2$ as the "local" part, meaning that it will serve as pseudopotential for all the $\ell \geq 2$ components. Minimization of the curvature of the (screened) pseudopotential at the origin (see Ref. [3]) was imposed as the additional requirement. The resulting pseudopotential is shown in Figure 1 and, for easy use, we parametrized its components in terms of Gaussian functions, in exactly the same way as Bachelet, Hamann and Schlüter (BHS) did (Eqs. (2.21, 2.22) of Ref. [4]). The corresponding α_i, c_i and A_i coefficients are given in Table 1. In direct space (Fig. 1b) we see that all components of our potential form very smooth curves. In reciprocal space (Fig. 1a) it is clearly visible that, in the plane-wave formalism, the pseudopotential will produce rapidly converging results because all components of the pseudopotential vanish at $q > 7$ a.u.$^{-1}$.

Table 2. Electron energy levels of carbon calculated for a variety of electronic configurations, using the present pseudopotential, compared with the all-electron energies. For each atomic configuration the first row corresponds to the "all-electron" calculation, the second row to the pseudoatom results. Configurations are ordered according to decreasing eigenvalues. For the very first unstable negative-ion configuration, the positive eigenvalue of the occupied d-state has been determined by the phase-shift condition.

(a) used in reference [4] to derive the BHS potential for $\ell = 2$.

valence configuration	eigenvalues [eV]		
	$2s$	$2p$	$3d$
$s^{2.0}p^{2.0}d^{0.2}$	−11.196	−3.097	1.074
	−11.216	−3.137	1.074
$s^{2.0}p^{2.0}d^{0.0}$	−13.613	−5.425	1.004
	−13.640	−5.464	1.004
$s^{1.0}p^{3.0}d^{0.0}$	−14.048	−5.825	0.995
	−14.093	−5.897	0.998
$s^{2.0}p^{1.5}d^{0.5}$	−17.904	−9.545	−0.195
	−17.929	−9.550	−0.195
$s^{1.5}p^{1.5}d^{0.5}$	−23.701	−15.260	−1.608
	−23.772	−15.257	−1.608
$s^{0.75}p^{1.0}d^{0.25}$ (a)	−41.592	−33.362	−9.394
	−41.827	−33.179	−9.352

3 Tests

We first checked the pseudopotential on atom, in various excited-state configurations, and the results are summarized in Table 2. The LDA with the Ceperley-Alder [5] form, parametrized by Perdew and Zunger, was applied throughout this paper as exchange-correlation potential in the Kohn-Sham equations, both in atomic calculations and on solid. The good agreement between the all-electron

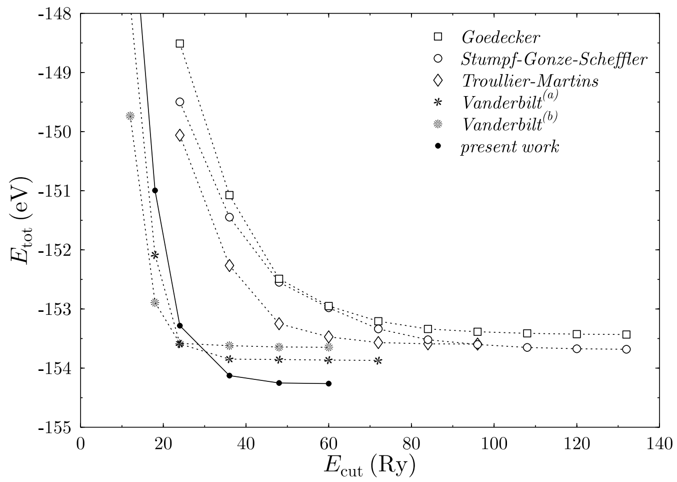


Fig. 2. Convergence of the total energy of diamond with plane-wave cutoff E_{cut}, compared for six types of pseudopotential. The symbols correspond to calculations of E_{tot} (per atom) at $a = 3.50$ Å, the connecting lines are guide to the eye. Two different Vanderbilt-type ultrasoft pseudopotentials correspond to different choices of the radii $r_{c,l}$, r_c^{loc} and r_0 (see Ref. [9]), *viz.* 1.25 ($l = 0, 1$), 1.10, 0.60 a.u.(a), and 1.40 ($l = 0, 1$), 1.30, 0.90 a.u. (b), respectively.

and pseudopotential eigenvalues, which is apparent from Table 2, in wide energy range and for various valence configurations, makes one to expect a good transferability of this pseudopotential to different crystal environments; we will return to this point later. A particularly good agreement can be observed for the *d*-states of an atom, the ones that correspond to the "local" *d* component of the potential. The pseudopotential actually used in all the tests on atom was reconstructed from the parameters listed in Table 1; this explains why the energy levels in the ground state configuration are not strictly identical with the all-electron calculations, as one would expect.

In order to test the performance of the pseudopotential in a solid we started by evaluating the (absolute) energies of diamond, at $a = 3.50$ Å – in plane-wave basis, and using the same LDA formalism [6] – as a function of the plane-wave cutoff E_{cut}; the results are shown in Figure 2. In this test the translational unit cell of diamond structure was chosen to be cubic (eight atoms per cell), and a single **k**-point (Γ) was used for the Brillouin zone integration. For comparison, we report in Figure 2 the results obtained with several other pseudopotentials that are nowadays currently used, *viz.* the Troullier-Martins [3] (TM), Goedecker [7] (GOE), and Stumpf, Gonze, Scheffler [8] (SGS) norm-conserving pseudopotentials, as well as with two constructions of the ultrasoft pseudopotential of Vanderbilt [9] (VDB).

The SGS pseudopotentials reference [8] are, essentially, a ghost-free variant of the well-known BHS pseudopotentials [4], that are adapted for use with the Kleinman-Bylander decomposition for calculation of non-local matrix elements. As the same core-radii and the same electronic configurations were used for their generation, the plane-wave convergence properties of the SGS and BHS pseudopotentials will be considered identical.

The two different ultrasoft VDB pseudopotentials to which we refer in Figure 2 correspond to two different choices of the core-radii and of the other "internal" parameters: the VDB(b) is the softest, the VDB(a) is somewhat harder – still in the ultrasoft category – and, presumably, more precise.

The absolute energies in Figure 2 are plotted as long as they vary by more than 0.001 eV/atom from one cutoff to the next (higher by 12 Ry).

One can distinguish in Figure 2 two types of behavior:

1) with the hardest and the most accurate pseudopotentials (the SGS-BHS and GOE), the absolute energy varies with E_{cut} slowly and the convergence is achieved only at around ≈ 120 Ry;
2) At the other extreme, with the ultrasoft Vanderbilt pseudopotentials, the energy gets "stabilized" already with small number of plane-waves, typically between 20 and 40 Ry.

While the behavior of the Troullier-Martins pseudopotential falls between the two types, Figure 2 suggests that the convergence properties of our present pseudopotential are closer to the ultrasoft family rather than to the other norm-conserving constructions.

It may be opportune to recall that the present pseudopotentials are norm-conserving as well – which has a certain value in their implementation and in use; the simplicity is further augmented when the Kleinman-Bylander decomposition is employed because, as one quickly discovers, the pseudopotential defined by Table 1 does not produce any ghost states.

Achieving convergence of the absolute energies amounts to requiring more than usually needed, because in most applications only the relative energies are sought: an energy difference of two systems, between two atomic configurations, or the form of energy-variation with a parameter. As the next step we thus tested the convergence of the calculated relative energies and, in particular, their accuracy. The test-quantities selected: the static equilibrium of the diamond structure (energy at the minimum (E_0), lattice constant (a_0), bulk modulus (B_0), pressure derivative of B_0 (B')), and the frozen phonon frequency of the TA(X) mode. In this test we use as gauge the BHS pseudopotential which, probably, is the best known "standard" and which counts to the most accurate pseudopotential schemes. These calculations were performed on the primitive translational unit of diamond structure (2 at./cell), using the 10 **k**-point sampling of Monkhorst-Pack, and without employing the Kleinman-Bylander decomposition; the frozen phonon calculations are performed on a tetragonal unit cell (volume $a_0^3/2$ (calculated static equilibrium), 4 at./cell) and with three "special" *k*-points. In this test we have calculated the total energy of diamond for 8 different values of lattice constant a varying between 3.20 and 3.70 Å, and fitted the resulting $E_{\mathrm{tot}}(V)$ by the Murnaghan equation of state. The results obtained with different plane-wave cutoffs, are summarized in Table 3.

Table 3. Convergence of selected ground-state properties with the increasing plane-wave cutoff: the value of the energy per atom at the minimum E_0, equilibrium lattice constant a_0, bulk modulus B_0, and its pressure derivative B' were obtained through a fit by Murnaghan equation of state; $\nu_{\mathrm{TA(X)}}$ is the frequency of the frozen phonon TA(X). The analogous results obtained with the BHS pseudopotential (Ref. [4]) are given for comparison.

	E_0 [eV]		a_0 [Å]		B_0 [Mbar]		B'		$\nu_{\mathrm{TA(X)}}$ [THz]	
E_{cut} [Ry]	present	BHS	present	BHS	present	BHS	present	BHS	present	BHS
24	−155.38		3.50		5.69		2.40		24.61	23.49
36	−156.13	−153.55	3.51	3.63	4.38	5.02	3.13	1.01	24.18	23.37
48	−156.24	−154.51	3.50	3.55	4.64	4.99	3.13	2.63	24.22	23.52
60	−156.25	−154.97	3.50	3.55	4.62	3.99	3.18	3.78	24.23	23.51
72		−155.28		3.54		4.88		2.69		
exp.			3.567		4.43				24.2	

After all what has been said, it does not come as big surprise finding that Table 3 shows comparable accuracy for both sets of "predictions" – all results are within the error range usual for the LDA calculations – and that it demonstrates a faster convergence of static equilibrium when our present scheme is used. Taking into account that alone fitting the $E(V)$ by an equation of state introduces a small uncertainty in the equilibrium values (of the order $\approx 1\%$ in a_0, and at least $\approx 3\%$ in B_0), the Table 3 demonstrates that fully converged results are obtained at $E_{\mathrm{cut}} \leq 36$ Ry.

The accuracy and the convergence of energy differences is further tested on the frequency of the frozen phonon TA(X) in diamond. This particular phonon is known [10] to be extremely sensitive to the energy cutoff used because of cancellation of different contributions to E_{tot}; this "probe" is a very stringent test of the accuracy of total energy calculations of any sort. Table 3 and Figure 3a demonstrate a complete convergence of this quantity at $E_{\mathrm{cut}} = 36$ Ry, and an excellent agreement with the experimental value, when the present pseudopotential is used.

As the last test we follow the behavior of pressure $p \equiv \partial E_{\mathrm{tot}}/\partial V$. Calculating pressure is an alternative way of establishing static equilibrium (the condition $p(a) = 0$), and this test brings us back to the "absolute" quantities belonging to the same category as *e.g.* the absolute energy in Figure 2. The derivative $\partial E_{\mathrm{tot}}/\partial V$ offers a probe that is even more sensitive to the size of the basis set than the energy alone (see *e.g.* Ref. [11]), and the variation of p shows in a strongly enhanced form the differences that, in principle, were apparent already in Figure 2. In Figure 3b we have thus plotted the variation $p(E_{\mathrm{cut}})$, calculated for different E^{pw} at the fixed $a_0 = 3.57$ Å, with the aid of the stress theorem [12]. This formula is analogous to the well-known Hellmann-Feynman theorem, and the pressure is obtained directly from the self-consistent potential and the charge density.

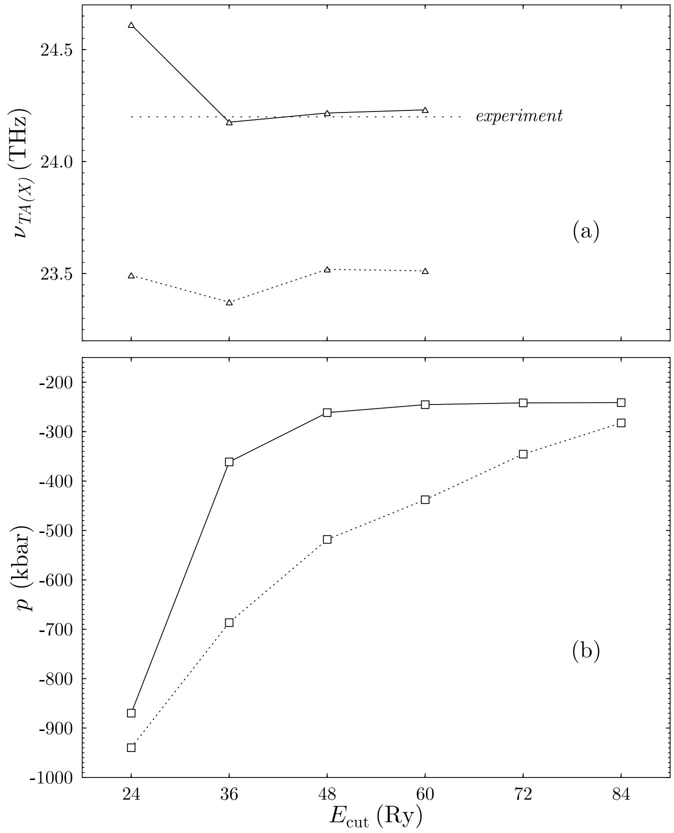


Fig. 3. Convergence with plane-wave cutoff of the frequency of the frozen phonon TA(X), and of the pressure calculated at (fixed) lattice constant $a_0 = 3.57$ Å, using the present carbon pseudopotential (solid lines). The analogous variations obtained with the BHS pseudopotential are shown for comparison (dotted lines).

Compared to the calculation using the BHS pspt., the much faster convergence of $p(E_{\mathrm{cut}})$ is immediately apparent in Figure 3b, and we note that the results obtained with both pseudopotentials agree at very high cutoffs E_{cut}, when both calculations become converged. Besides clearly documenting the accuracy, the variations $p(E_{\mathrm{cut}})$ and $\nu(\mathrm{TA(X)})$ shown in Figure 3 are the most rigorous of all the convergence tests shown in this work.

Besides "softness" and accuracy in predicting measurable quantities, another important quality of a good pseudopotential is its transferability: the validity in other crystal environments and, namely, with different types of bonding. Although a thorough test of transferability would be beyond the scope of this short note, we can report the structural result we obtained with the present pseudopotential in graphite: the in-plane lattice constant $a = 4.59$ Å (1.3% under the experiment). The result for a suggests that the present pseudopotential performs well in the description of the sp^2 bonds as well; its application to fullerenes, nanotubes, etc. can thus be envisaged. We also note that the present pseudopotential was applied in reference [13], with success, to calculation of one-electron energies, pseudowavefunctions and densities of states (DOS) of graphite. In reference [13], both σ- and π- calculated densities of states were found in a very good accordance with measured K-polarized bands. Additionally, the calculated band structure is consistent with the recent review of electronic band structure calculations of graphite [14].

It remains to hope that future applications of the pseudopotential introduced here to many different physical problems will establish the transferability in an exhaustive manner.

4 Conclusions

We have presented a norm-conserving pseudopotential for carbon that rapidly converges in reciprocal space, and demonstrated that convergence of total-energy related quantities with number of plane waves can be achieved at the cutoff energies of order $E_{\text{cut}} = 36$ Ry – which is comparable with the performance of the ultrasoft Vanderbilt pseudopotentials. The pseudopotential is given in an l-dependent form, and parametrized in the same way as the well-known Bachelet-Hamann-Schlüter pseudopotentials. When transformed into the Kleinman-Bylander form, the present pseudopotential does not lead to any ghost states. Applying this scheme in material science and organic chemistry will significantly facilitate all calculations employing plane waves as basis set.

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References

1. J. Vackář, A. Šimůnek, Solid State Commun. **81**, 837 (1992).
2. "Generalized" indicates that potential can be created at an arbitrary reference energy, not only for energies of atomic bound states. See D.R. Hamann, Phys. Rev B **40**, 2980 (1989).
3. N. Troullier, J.L. Martins, Phys. Rev. B **43**, 1993 (1991).
4. G.B. Bachelet, D.R. Hamann, M. Schlüter, Phys. Rev. B **26**, 4199 (1982).
5. D.M. Ceperley, B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
6. J. Ihm, A. Zunger, M.L. Cohen, J. Phys. C **12**, 4409 (1979).
7. S. Goedecker, M. Teter, J. Hutter, Phys. Rev. B **54**, 1703 (1996); C. Hartwigsen, S. Goedecker, J. Hutter, Phys. Rev. B **58**, 3641 (1998).
8. R. Stumpf, X. Gonze, M. Scheffler, Fritz-Haber-Institut Res. Rep (April 1990).
9. D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
10. See *e.g.* Figure 12 in K. Kunc, P. Gomes Dacosta, Phys. Rev. B **32**, 2010 (1985); and the discussion in C. Falter, M. Selmke, W. Ludwig, K. Kunc, Phys. Rev. B **32**, 6518 (1985).
11. P. Gomes Dacosta, O.H. Nielsen, K. Kunc, J. Phys. C **19**, 3163 (1986).
12. O.H. Nielsen, R.M. Martin, Phys. Rev. Lett. **50**, 697 (1983); Phys. Rev. B **32**, 3780 (1985).
13. G. Wiech, N. Auer, A. Simunek, J. Vackar, A. Hammerschmidt, G. Rittmayer, Diamond and Related Mater. **6**, 944 (1997).
14. J.C. Boettger, Phys. Rev. B **55**, 11202 (1997).
15. We have used the code CPMD, version 3.0, developed by J. Hutter, P. Ballone, M. Bernasconi, P. Focher, E. Fois, S. Goedecker, M. Parrinello, M. Tuckerman, at Max Planck Institut für Festkörperforschung, Stuttgart, and IBM Zurich Research Laboratory (1990-1996).